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Effects of C, Cu, and Be substitutions in superconducting MgB_2

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Density functional calculations are used to investigate the effects of partial substitutional alloying of the B site in MgB_2 with C and Be alone and combined with substitution of Mg by Cu. The effect of such substitutions on the electronic structure, electron-phonon coupling, and superconductivity are discussed. We find that Be substitution for B is unfavorable for superconductivity as it leads to a softer lattice and weaker electron-phonon couplings. Replacement of Mg by Cu increases the lattice stiffness and electron count. We estimate that with full replacement of Mg by Cu and fractional substitution of B by C, T_c values of 50 K may be attainable.

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The discovery of superconductivity with critical temperature $T_c = 39$ K in MgB_2 has led to considerable interest in this material, both for applications and from a fundamental point of view.[1] Although it is not the highest T_c conventional (in the sense of s wave with likely substantial electron-phonon coupling) superconductor,[2] its substantial T_c combined with its chemistry and other properties may make it particularly useful.[3–5] Various measurements, including B isotope effect,[6] phonon densities of states,[7,8] tunneling,[9] transport,[3,10,11] and specific heat,[12,13] have been done. Taken together, they yield a clear picture of MgB_2 as a conventional electron-phonon s-wave superconductor, consistent with most theoretical work. Ripplinger[14] discussed the electronic structure and bonding using density functional calculations with the linearized augmented planewave (LAPW) method. The band structure was consistent with an early calculation.[15] Several authors have extended this work presenting the electronic structure in detail and discussing the origin of superconductivity.[16–21] The band structure is dominated by chemical bonding in the hexagonal B sheets in MgB_2. Although the nominal electron count is the same as in graphite (Mg has nominal 2^+ charge), the top of the B derived σ bonding band structure contains holes. The negative charge of the B layers and the corresponding positive charge of the Mg layers plays a role in raising the in-plane σ orbitals relative to E_F as compared to graphite.[16] Kong *et al.* and Bohnen *et al.* reported electron-phonon calculations over the whole zone obtaining couplings consistent with the measured T_c as well as the boron isotope effect, the specific heat enhancement, the reported gap values, and transport data.[17,18] They show strong coupling between the hole ''doped'' bonding bands and high frequency optical phonons associated with motions of the B atoms affecting the covalent bonds.

The picture that emerges is one where the high T_c is due to strong electron-phonon coupling associated with the hole doped metallic σ bonding bands in the B sheets. The light B mass is responsible for the high average frequency of the strongly coupled phonons, setting the temperature scale. The crucial aspects for the superconductivity seem to be (1) band structure, particularly the presence of hole doped σ bands at the Fermi level, E_F, (2) strong electron-phonon coupling associated with the strong covalent bonding nature of these bands, and (3) high phonon frequencies associated again with the strong covalent bonds and the light B mass.

Here we explore some possible substitutions and give a suggestion for experimental work aimed at finding related high T_c phases. Along these lines, Medvedeva *et al.* investigated a number of possible substitutions of Mg by monovalent, divalent and trivalent ions.[20] They focused on the band structure, particularly the density of states (DOS) and presence or absence of the σ band at E_F. They concluded that trivalent substitutions like Y, Al, etc. are not favorable as they fill the hole doped (in MgB_2) σ bands, while certain monovalent substitutions for Mg may be favorable. This is consistent with the experimental observation that Al substitution destroys superconductivity.[22] They also mentioned possible vacancies or substitutions in the B sheets, but concluded that these are all unfavorable. We briefly examine Be substitution in the sheets. Though Be lowers the electron count, superconductivity is suppressed due to a strong decrease in the lattice stiffness and a drop in the electron-phonon coupling. We then report calculations investigating the effect of a combined partial substitution of C for B and Cu for Mg. The rationale for this is that very strong C-B bonds are expected in this structure, so C substitution may lead to a stiffening of the sheets relative to MgB_2, while the replacement of Mg by Cu may be expected to first of all compensate for the extra charge provided by the substitution in the plane, and second, maintain the hole doping of the σ bonding band, present in MgB_2 but absent in graphite, due to crystal field effects from Cu d–B p hybridization. We find that this is so and that for modest C incorporation and Cu replacement of Mg superconductivity should be enhanced. Based on rigid muffin tin approximation (RMTA) calculations, we estimate that T_c may be near 50 K.

Our results were obtained in the local density approximation[23] (LDA) with the LAPW method, including local orbitals,[24,25] and well converged basis sets and zone samplings. Band structures, lattice stiffnesses, and electron-phonon couplings were determined at the calculated lattice parameters from energy minimization. LDA calculations often slightly underestimate lattice constants. For MgB_2 we get $a = 5.736a_0$ and $c = 6.522.a_0$, as compared to the experimental values $a = 5.826a_0$ and $c = 6.653a_0$. This is a 5% volume compression. As shown in Fig. 1, this has a very small effect on the band structure near the Fermi energy E_F with a small effect on $N(E_F)$. To proceed to alloys and superconductivity, we make three more significant approximations. First of all,

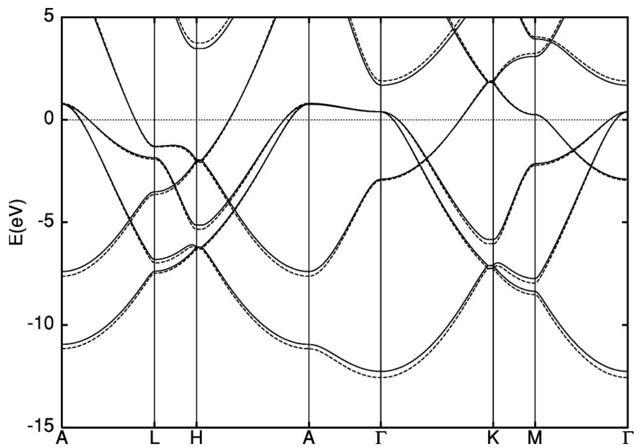

FIG. 1. LDA band structure of MgB_2 with the experimental structure (solid) and calculated LDA lattice parameters (dashed). The zero is at E_F.

we employ the virtual crystal approximation (VCA) to account for partial substitutions on the B sheets. A partial justification for this is provided by the strong covalency and corresponding large bandwidths, which may limit the amount of scattering due to potential disorder in the alloy (this is the same effect that allows alloys, like $Al_xGa_{1-x}As$, to have high enough mobilities to be useful in semiconductor technology). We tested the VCA by comparing with ordered cells at the compositions MgBeB and CuBC and found some quantitative differences, but the key features of the band shapes, velocities, and the position of the σ bonding band relative to E_F were little changed. The second approximation we made was to characterize the lattice stiffness by the calculated tensile stiffness of the B sheets, i.e. $\partial^2 E/\partial a^2$. The variation of this number and the composition dependent mass of the sheets was used to scale the average frequencies as calculated by Kong *et al.*[17] We use an average phonon frequency of 850 K for MgB_2. Considering that the dominant phonons determining T_c are the B modes, we think that this is a reasonable approximation. Finally, we use the RMTA to characterize the electron phonon coupling.[26,27]

We used DOS calculations from first principles eigenvalues at over 2000 **k** points in the irreducible zone for $N(E_F)$ and the angular momentum components, and the self-consistent LAPW potentials at different concentrations to calculate the corresponding phase shifts and free scatterer DOS. Sphere radii of $1.5a_0$ were used for B, Be, and C in the RMTA calculations. The above quantities were used in the Gaspari-Gyorffy formula to compute the Hopfield parameters, η, for each site. Negligible coupling is found on the Mg site, as expected, but not Cu, e.g., 0.78 $\mathrm{eV/Å^2}$ on Cu for CuB_2. However, in Table I we give the values of η for B only, since that is the dominant contribution controlling superconductivity and we do not include any Cu contribution in the calculation of λ or T_c (Cu will have little involvement in the high frequency phonons associated with the B sheets). For the electron-phonon coupling we used the usual expression $\lambda = \eta/\langle M\omega^2\rangle$. In the denominator we used the average frequency of Kong *et al.*[17] for MgB_2 and scaled it using the tensile stiffness of the B sheets for various concentrations,

TABLE I. Properties of $MgBe_xB_{2-x}$ and $CuB_{2-x}C_x$ as obtained in the VCA. S is the relative stiffness of the sheets characterized by $\partial^2 E/\partial a^2$ ($S(MgB_2)=1$), and the other symbols have their usual meanings. Lattice parameters are in a_0, $N(E_F)$ in eV^{-1}, and T_c in K. The unscaled η (in $\mathrm{eV/Å^2}$) is for the alloyed B site only. Blank entries for a, c, and S indicate that these were from interpolation rather than direct computation for those concentrations. λ^* and T_c^* are values calculated using the alternate scaling of η by a factor of 2 as discussed in the text. Note the insensitivity of T_c to this scaling.

	a	c	S	$N(E_F)$	η	λ^*	T_c^*	λ	T_c
MgB_2	5.74	6.52	1.00	0.68	3.60	0.93	39	0.78	38
$MgBe_{0.5}B_{1.5}$	5.99	6.54	0.78	0.84	2.36	0.78	26	0.66	22
MgBeB	6.43	6.03	0.56	0.90	1.45	0.67	16	0.56	12
$MgBe_{1.5}B_{0.5}$	6.90	5.53	0.48	0.98	1.04	0.56	9	0.47	6
$MgBe_2$	7.32	5.34	0.47	0.95	0.93	0.52	7	0.43	4
CuB_2	5.58	6.28	1.11	1.09	4.38	1.02	48	0.86	48
$CuB_{1.75}C_{0.25}$				0.83	5.16	1.08	54	0.90	55
$CuB_{1.5}C_{0.5}$	5.37	6.56	1.37	0.65	5.45	1.03	53	0.86	53
$CuB_{1.4}C_{0.6}$				0.50	3.74	0.68	24	0.57	20
$CuB_{1.25}C_{0.75}$				0.25	0.80	0.14	0	0.12	0
CuBC	5.11	7.28	1.63	0.40	1.02	0.16	0	0.14	0

i.e., $\partial^2 E/\partial a^2$. The RMTA is not generally as well justified in sp metals as in transition metals and can considerably underestimate the deformation potentials when strong sp covalent bonding is present as it is here. Further, the RMTA neglects some differences between different bands, which may be significant here. In any case, Kortus *et al.* did use it for MgB_2 to characterize electron-phonon couplings.[19] Our RMTA value of η for MgB_2 is significantly lower than that of Kortus *et al.* We do not understand the reason for this difference, but note that their calculations were done with overlapping ASA spheres. We obtain much better agreement with a subsequent calculation by Antropov *et al.*[21] Comparing with the direct calculations of Kong *et al.* for MgB_2 we find, not unexpectedly, that the values of η we obtain with our nonoverlapping B spheres are too small, roughly by a factor of 3. Here we

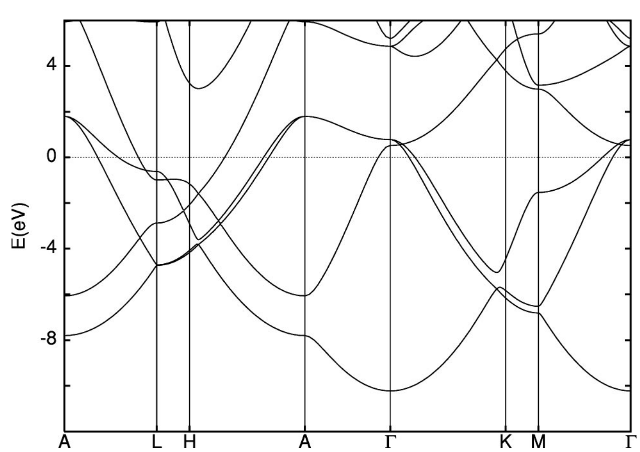

FIG. 2. LDA virtual crystal band structure of $MgBe_xB_{2-x}$ for $x=1$. The lattice parameters are the calculated relaxed values. The horizontal reference at 0 denotes E_F.

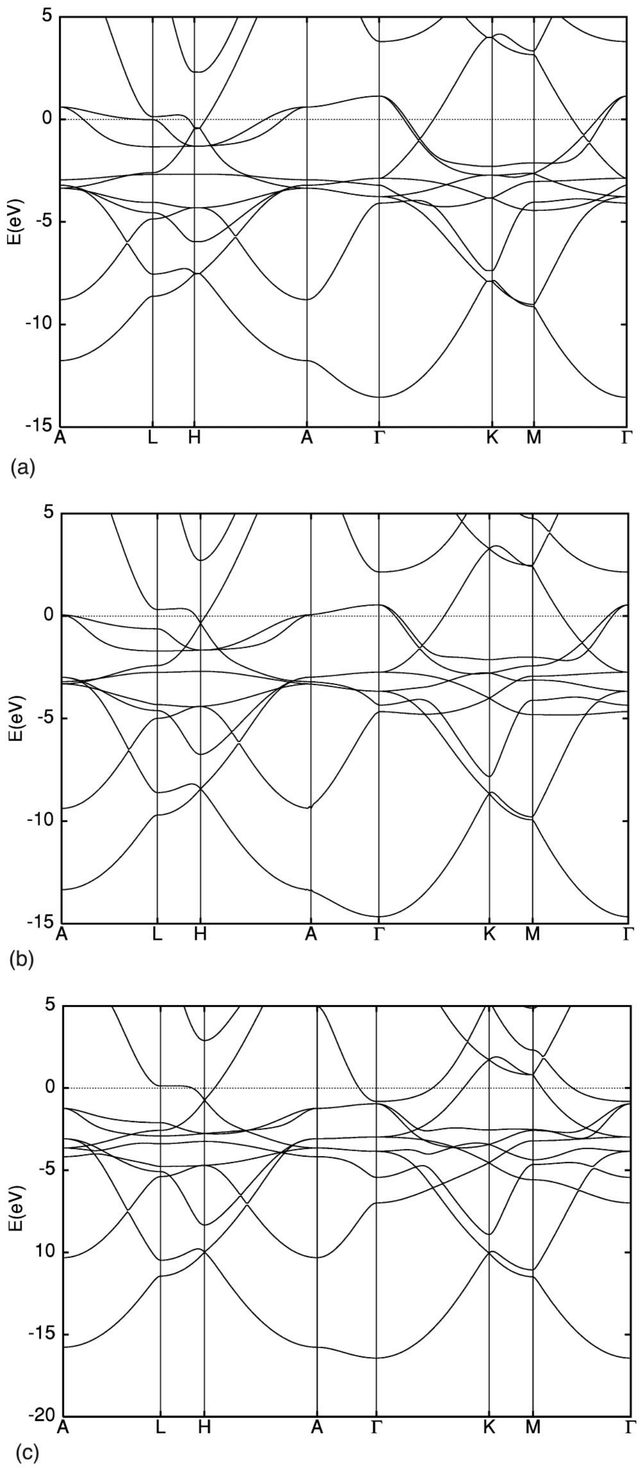

FIG. 3. LDA virtual crystal band structures of $CuB_{2-x}C_x$ for $x=0$ (top), $x=0.5$ (middle), and $x=1$ (bottom). The lattice parameters are the calculated relaxed values. Note the vertical scale of the lower panel. The horizontal reference at 0 denotes E_F.

use the RMTA to elucidate trends, while acknowledging its limitations. We adopt the heuristic of scaling the calculated values of η by 3 in calculating λ and T_c. Using the average phonon frequencies quoted by Kong *et al.*, this heuristic closely reproduces their values of λ and T_c for MgB_2. We used the McMillan equation to roughly estimate T_c, setting the Coulomb pseudopotential $\mu^*=0.1$. We emphasize here that we are not aiming at an accurate determination of the value of T_c but exploring the trends upon substituting Mg by Cu and B by Be or C. If instead, we restrict the scaling of η to a factor of 2 and adjust the average phonon frequency to get $T_c=39$ K for MgB_2 we would need $\langle\omega\rangle=635$ K, which is unreasonably low. Even so, the trends in T_c for the various compounds would be little changed (see Table I).

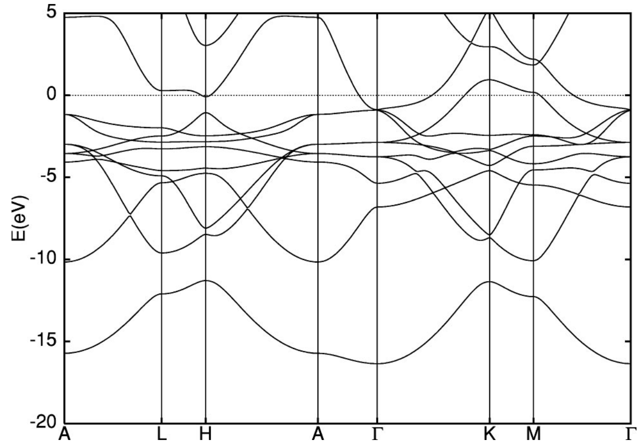

FIG. 4. LDA ordered band structure for CuBC. Note the splittings relative to the virtual crystal band structure in the bottom panel of Fig. 3.

Our band structure for MgB_2 (Fig. 1) is practically identical to prior results,[28] showing σ bonding states at E_F. Results for the structural and electronic properties relevant to superconductivity are given in Table I, while band structures are shown in Figs. 2 and 3 for $MgBe_xB_{2-x}$ and $CuB_{2-x}C_x$, respectively. In the table the values of η are the bare values as given by the RMTA; scaled values are given for λ and T_c (λ^* and T_c^* scaling η by 2 instead of 3). An ordered band structure for CuBC is shown in Fig. 4. This shows some differences from the corresponding VCA calculation, most notably, near E_F, a splitting at the H point involving p_z bands. However, the general structure of bands near E_F and the position of the σ band is quite similar.

Substitution of Be into the sheets lowers the electron count, though not in a rigid band way. The hole concentration in the σ bonding band does increase, but the bonds are strongly weakened. This is seen in the bandwidths and lattice stiffness. The result (Table I) is a rapid increase in a, softening of the lattice, and a decrease in the electron-phonon coupling. Thus Be substitution is detrimental to superconductivity.

The Cu substituted material is more interesting. In an ionic model, replacement of Mg by monovalent Cu should lower the sheet electron count by one per formula unit. However, the result differs from in-sheet Be substitution. The Cu is nominally monovalent as in the ionic model. The five narrow Cu d bands are in the valence region between -4 and -3 eV relative to E_F. However, there is noticable Cu d–B p hybridization, and the bands up to E_F have partial Cu character. This is reflected in the nonzero values η associated with the Cu site. Comparing the top panel of Figs. 1

and 3 and the structural information in Table I one sees that the in-sheet bonding is strengthened by Cu substitution, even though the hole count in the σ band is increased (note the relative positions of the band maxima on the Γ-A line). Hybridization with Cu yields quantitative band structure changes, affecting mostly the p_z states, but there are also weak effects on the σ bands near E_F, e.g., the reversed dispersion on the Γ-A line due to $d-p\pi$ interactions. The net effects of Cu substitution—stiffened lattice, increased $N(E_F)$ and higher hole concentration—are favorable for superconductivity. Related to this, there is a recent unconfirmed report of an enhancement of T_c with partial replacement of Mg by Cu.[29] Partial substitution of C for B in CuB_2 has two effects—a stiffening of the lattice reflecting the strong bonding of C and B (favorable for T_c and a reduction in the hole doping of the σ band and in $N(E_F)$ (unfavorable for T_c). For low C concentrations, the first effect dominates, leading to an increase in the estimated T_c, but beyond 25% C substitution (here the van Hove from the σ band at A crosses E_F) the second dominates and T_c falls. Interestingly, λ changes more slowly than η over the high T_c range. This reflects the role of bonding in the electron-phonon coupling. All things being equal, stronger bonding increases η but also the lattice stiffness, which is the denominator of λ. Meanwhile, the prefactor of the MacMillan-Dynes formula is increased.

In summary, our calculations suggest that the T_c of MgB_2 can be increased, perhaps to 50 K by substitution of Cu for Mg and low C substitutions, around 25%, in the B sheets. To our knowledge, CuB_2 in this structure does not exist. However, while we cannot show that $Cu(B,C)_2$ exists, C alloying strengthens the sheets and so the alloy may be stablized.

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